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Improvement in Precision of Polarographic Analysis

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SINCE the photorecording system was introduced in polarography, numerous papers have interpreted photorecorded polarograms, but no definite conclusion has been reached as yet with respect to the degree of accuracy that can be expected in measuring these curves.

Buckley and Taylor (*2*) estimated that the value of i_d (diffusion current) is reproducible within the limits of 0.5 and 4%, whereas Mueller (*11*) believes that an accuracy of $\pm 1\%$ can be reached by using averages of several polarograms of the same solution. To minimize these errors Jablonski and Moritz (*6*) suggest the use of an accurate measuring microscope for determining the wave height, and Baumberger and Bardwell (*1*) recommend the drawing of abscissas on the photographic paper by the help of an additional lamp, in order to facilitate a direct reading of the applied voltage.

Probably as a consequence of these uncertainties, Kolthoff and Lingane (*7*), Zlotowski and Kolthoff (*14*), and Lingane and Meites (*10*) depart from the use of the more convenient polarograph and prefer manual measurements, in order to attain maximum precision.

It appears that sufficient emphasis has not been placed on errors arising from the photorecording of polarograms and their measurement. Continuous dimensional changes of the photographic paper itself under the influence of changes in the relative humidity of the surrounding air (R.H.) have been reported (3–5) to amount to as much as 2.5% of its width and 0.5% of its length.

Investigations were therefore undertaken to determine the extent of dimensional changes occurring at different degrees of relative humidity for the particular type of photographic paper recommended for polarographic work, to study the influence of these variations upon the accuracy of measurements on polarograms, and to devise methods to minimize these errors.

EXPERIMENTAL

A Model XII Heyrovský polarograph and Kodak bromide paper F-1, 15.2 × 25.4 cm. were used for the investigations. Strips of the paper 3 cm. in width were cut parallel to the smaller side of the sheets. Each strip was placed in a glass cylinder 60 mm. in diameter and 130 mm. in height, and a slow stream of air with a known moisture content was passed over it. The air was analyzed for its moisture content by a Serdex Boston hygrometer, Model 201, with a reported precision of ±1%. The rate of flow was measured by a calibrated flowmeter. The flow was kept at a low value in order to approach conditions to which polarograms actually may be exposed. The dimensional changes were registered. The accompanying changes in moisture content were measured by weighing in a small (15-cc.) covered weighing bottle. All transfers were made as rapidly as possible.

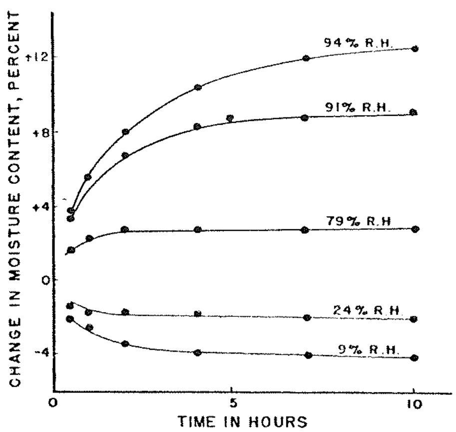

Figure 1. Change in Moisture Content of Undeveloped Photographic Paper at Different Degrees of Relative Humidity

Paper seasoned at 52% R.H. prior to determination. Flow of air, 300 cc. per minute. Temperature 28° ± 0.5° C.

The shrinkage and expansion of a recorded polarogram on a full size sheet of photographic paper were determined under similar conditions. No temperature control was used, but the temperature did not vary more than 1° C. during a series of experiments.

Dimensional changes as well as the change in moisture content of the paper were also determined over a number of water–sulfuric acid mixtures in desiccators.

In all cases the paper under investigation was conditioned with air of known relative humidity prior to the experiment. The length of the strips was measured always at the same place, as slight deviations in dimension were observed at different sections of the paper.

DIMENSIONAL CHANGES IN PAPER

Changes between Dry and Wet State under Extreme Conditions. A developed sheet of photographic paper was dried in a calcium chloride desiccator for a week. The width and length of the paper were measured; then the paper was thoroughly moistened by immersing in water at room temperature for 15 minutes and freed from excessive moisture by means of a blotter. The width and length were again measured. The expansion observed from the dry to the wet state was 4.3% in width and 1.6% in length.

The results show that under these conditions dimensional variations of a considerable magnitude occur in either direction. It follows that under similar conditions the accuracy of measurements on polarograms will be seriously affected with regard to both wave height and half-wave potential.

As the change in width was found to be nearly three times the change in length, the effect of variations in relative humidity upon the width and the accuracy of wave height measurements was selected for a detailed study.

INFLUENCE OF HUMIDITY OF AIR

Influence upon Moisture Content and Width of Undeveloped Photographic Paper. The rate of adsorption and desorption as well as expansion and shrinkage in the width of undeveloped photographic paper was determined under a slow stream of air with known moisture content. Figures 1 and 2 show the results obtained.

The values of width in Figure 2 reached after 10 hours are plotted in Figure 3 compared with those obtained from determinations on developed paper, using the same experimental procedure.

Figure 4 shows the rate of adsorption and expansion in width of undeveloped photographic paper in a quiet atmosphere (desiccator) of 84% relative humidity.

The changes in width on samples of undeveloped paper were then measured at different degrees of relative humidity in the same way, at the end of 51 hours. A maximum deviation of 2.8% was found between the width of the paper at 14 and at 92.5% relative humidity; the points in between formed an S-shaped curve similar to the ones given in Figure 3.

Results of the following qualitative test clearly show that these

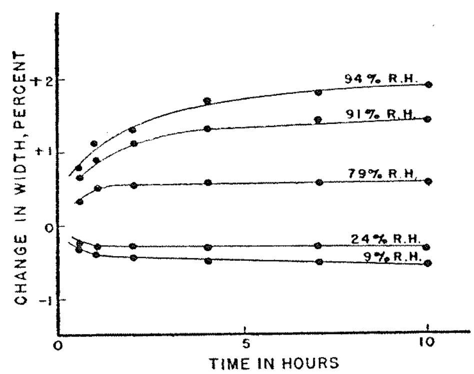

Figure 2. Change in Width of Undeveloped Photographic Paper at Different Degrees of Relative Humidity

Paper seasoned at 52% R.H. prior to determination. Flow of air, 300 cc. per minute. Temperature 28° ± 0.5° C.

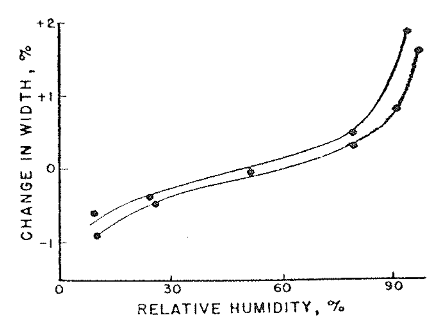

Figure 3. Change in Width of 3-Cm. Strips of Photographic Paper with Changing Relative Humidity

Flow of air, 300 cc. per minute. Seasoned at 52% R.H. in desiccator.
Upper. Undeveloped paper, temperature during experiment 28° ± 0.5° C.
Lower. Developed paper, temperature 25° ± 0.5° C.

The effect of relative humidity of air upon the dimensional changes of photorecorded polarograms has been investigated. A method is described for minimizing this error. The procedure consists of photographing two parallel lines, which serve as a comparative scale, on the photographic paper at the time the polarogram is taken. This method increases the precision of wave height measurements about 25-fold.

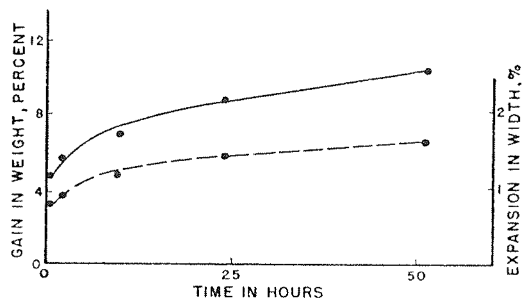

Figure 4. Rate of Adsorption and Expansion in Width of Undeveloped Photographic Paper

Quiet atmosphere at 84% R.H. and 26° ± 1° C. (desiccator)
Pretreatment of paper, 4 days over calcium chloride in desiccator
Solid line, gain in weight
Broken line, expansion

variations in width of undeveloped paper actually influence the accuracy of polarograms when taken at different degrees of relative humidity.

The camera was loaded and inserted into the polarograph. Without removing the camera, a stream of air (95% relative humidity) was passed through it for 17 hours by means of a rubber tubing leading into the interior of the inner cylinder through the small space left free at the end of the paper-retaining bar. The rubber tubing was then detached. The camera was made ready for exposure as usual. Lines were drawn photographically at settings of 5, 75, and 145 mm., respectively, of the galvanometer light beam on the visual scale. The lines were run from settings 3 to 4.5 on the camera drum. Then the shutter was closed. The procedure described above was repeated, using air of 15% relative humidity, and passing this air through the camera for 5 hours. Lines were drawn from settings 4.5 to 6 on the camera drum, again at settings of 5, 75, and 145 mm., respectively, of the light beam on the visual scale. The temperature during the experiment was 25° ± 0.5° C. Figure 5 shows the photograph obtained.

Influence upon Moisture Content and Width of Developed Photographic Paper. Under the same experimental conditions as in the determinations with undeveloped paper, the type of adsorption and desorption as well as the type of expansion and shrinkage of the developed paper was found to be identical with that observed with the undeveloped paper under a slow stream of air. Figure 3 shows the changes in width of the developed paper after a 10-hour exposure to air of different degrees of relative humidity compared to the behavior of undeveloped paper.

Aside from variations in moisture content and width at different degrees of relative humidity, the width of developed paper was found to be smaller by 0.33% than at the same degree of relative humidity in the undeveloped state. The shrinkage was measured on five samples after seasoning at 52% relative humidity.

The change in width of developed paper in a quiet atmosphere was determined, using similar experimental conditions as with undeveloped paper. The maximum deviation in width between paper treated at 21 and 90% relative humidity, respectively, was found to be 1.7% after 51 hours of exposure.

To observe the behavior of developed paper under conditions to which a photorecorded polarogram might be exposed in normal practice, five samples of developed photographic paper were placed at a spot in the laboratory. The width was measured after 24 hours and, from then on, once a day for a week. In samples seasoned under a flow of air at 9.5, 26, 79, 91, and 97% relative humidity, respectively, for 10 hours prior to the test the deviation in width was found to be less than ±0.1% among the five samples at any date of measurement.

Figure 6 shows the range in which the relative humidity of the laboratory air changed during the one week's test, and the accompanying changes in width of the paper.

Influence upon Calculation of Diffusion Current from a Polarogram. MINIMALIZATION OF ERROR. A polarogram of copper in ammoniacal medium was prepared. Figure 7 shows the copper wave, *FC*, and the residual current, *GD*. At the same time this polarogram was taken, two additional ordinates were drawn on the photographic paper at constant settings of the light beam on the visual scale of the instrument, with the cell circuit open. The lines were at a distance of 140 mm. on this scale.

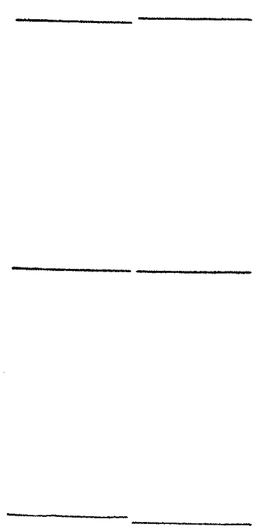

Figure 5. Displacement of Photographed Ordinates by Change in Relative Humidity

Lines obtained in either case at settings of 5, 75, and 145 mm. of light beam on visual scale. Lines on left after passing air of 95% R.H. through camera for 17 hours. Lines on right after passing air of 15% R.H. through camera for 5 hours

The polarograph had been calibrated previously according to the procedure given by Kolthoff and Lingane (*8*), using two precision resistances. The diffusion current was calculated from this polarogram according to the "graphical method" as well as the "exact method," suggested by Taylor (*13*) for absolute work in polarography (*12*). The exact method corresponds to the one suggested earlier by Kolthoff and Lingane (*8*).

Table I shows the values obtained according to the conventional methods, in Table II the values for the diffusion current are corrected. In this case the distance between the two ordinates was measured first and compared with the theoretical

Table I. Dependence of Calculated Diffusion Current upon Degree of Relative Humidity at Which Polarogram Was Seasoned[a]

Seasoning, % R.H.	Graphical Method Copper Wave Height, *FC*		Residual Current Wave Height, *GD*		Exact Method *FC* − *GD*
	Mm. obsd.	*µamp.*	*Mm. obsd.*	*µamp.*	*µamp.*
97	91.1	45.55	5.4	0.14	45.41
86	90.2	45.10	5.3	0.13	44.97
59	89.4	44.70	5.3	0.13	44.57
40	89.2	44.60	5.3	0.13	44.47
12	88.7	44.35	5.2	0.13	44.22

[a] See Figure 7. Shunt copper wave = 100, shunt residual current = 5, s^2 = 0.0050 µ amp./mm. on visual scale.

Table II. Elimination of Deviations in Size of Diffusion Current Caused by Changing Relative Humidity[a]

Seasoning, % R.H.	Distance between Ordinates, Mm.	$F = \frac{140 \text{ Mm.}}{\text{Distance between Ordinates, Mm.}}$	Diffusion current (FC to GD, μ amp.) $\times F$
97	138.5	1.0108	45.90
86	137.2	1.0204	45.89
59	136.3	1.0271	45.78
40	135.8	1.0309	45.84
12	134.9	1.0378	45.89
		Av.	45.86 ± 0.06 μ amp.

[a] See curve Figure 7. Shunt copper wave = 100, shunt residual current = 5. Two ordinates were drawn at a distance corresponding to 140 mm. on visual scale. s° = 0.0050 μ amp./mm. on visual scale.

distance of 140 mm. A factor, F, was thus obtained, which served to correct the diffusion currents calculated from the polarogram according to the exact method.

Inaccuracies of Photorecorded Polarograms Caused by Factors Other Than Humidity of Air. Lingane (*9*) reports a deviation of about 3.5% for the galvanometer deflection on the visual scale from the measurement on the photographic paper. An inaccuracy of the same order was observed in the present study, although the precise amount of this deviation was not determined.

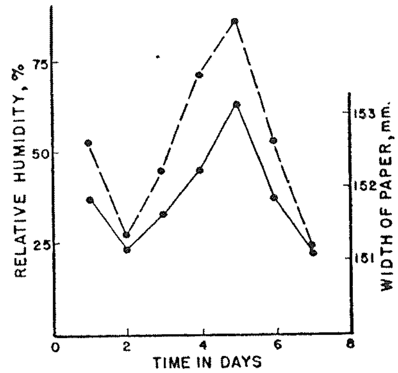

Figure 6. Daily Variation in Relative Humidity of Air in Laboratory

Concurrent variations in width of openly exposed developed photographic paper. Measurements of width (solid line) are average values from 5 samples each. Samples pretreated at 9.5, 26, 79, 91, and 97% R.H. for 10 hours

Although the source of this error if overlooked would affect the accuracy of wave height measurements considerably, a similar inaccuracy in the determination of the half-wave potential may arise from improper loading of the camera. It was noticed during the present investigation that lines drawn parallel to the width of the paper by moving the light beam over the visual scale at constant settings of the camera drum, were not recorded as parallels. Several sheets of paper were treated this way and examined. The perpendicular distance between any two lines was as much as 0.7% greater at the points corresponding to the zero value of the visual scale than at the opposite end. A change of only 0.25 mm. in distance of the surface of the photographic paper from the center of the camera would result in a deviation of this magnitude. Therefore, it is more than likely that the deviation originates in the construction of the paper-retaining bar, which probably tightens the photographic paper to the inner cylinder of the camera to a better degree at its hinged end than at the part containing the spring clip.

DISCUSSION

The data in Table I reflect the deviation in diffusion current calculated from one and the same polarogram, treated at different degrees of relative humidity. The error between 12 and 97%, respectively, is roughly 2.5%.

Table II shows that the influence of the relative humidity has been minimized to a great extent. In this case the slight deviations are mainly due to subjective errors in measurement. The deviation is only ±0.13%. Table II shows, furthermore, that not only the influence of the changing relative humidity but also the inaccuracies caused by instrumental shortcomings have been

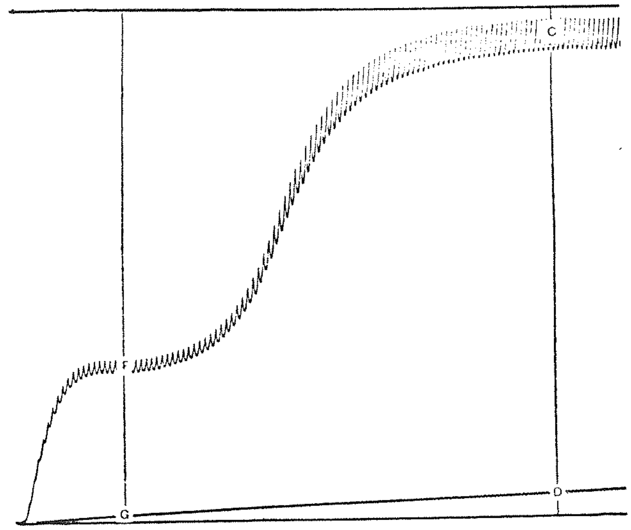

Figure 7. Polarogram of Copper in Ammoniacal Solution

Used for determining influence of R.H. on wave height and accuracy that can be obtained by drawing two parallel lines representing known current (Tables I and II)

reduced to a minimum. These latter inaccuracies would increase the error to 3.5% when wave heights were measured according to conventional methods and no correction was made. The combined error for influence of relative humidity and instrumental inaccuracy can be obtained by comparing the average value of the last column in Table II with those in columns 3 and 6 of Table I.

SUMMARY

The influence of the relative humidity of air ranging from 12 to 100% upon dimensions and moisture content of photographic paper used in polarographic work has been studied. The paper investigated responds quickly to sudden changes in relative humidity and approaches equilibrium values in width in about 4 hours under conditions similar to those to which polarograms are exposed in research and routine work. The dimensional changes of the paper are correlated with changes in moisture content, though not in a linear fashion.

The precision of wave height measurements is ±0.7% in the range between 30 and 75% relative humidity. Errors of greater magnitude up to 2.5% occur at humidities beyond these limits. An instrumental inaccuracy has been observed with the particular commercial polarograph used for this investigation increasing the over-all error to ±3.5% under unfavorable conditions. The inaccuracies observed in measuring the wave heights under defined experimental conditions have been verified in a series of tests corresponding to conditions which are encountered in the normal practice of polarographic work.

A simple method has been developed for minimizing the combined errors in measuring wave heights caused by varying relative humidity and instrumental inaccuracy. It consists of drawing two additional ordinates on the photographic paper at a known distance as a scale for calibration. The possible over-all error has been reduced thus from ±3.5 to ±0.13%.

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